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JOURNAL OF POLYMER SCIENCE, vol. 16, no. 2, February 1978, pages 483-490, John Wiley & Sons, Inc.; Y.K. KIM et al.: "Polycycloalkylene-siloxane polymers: Synthesis and thermal study"

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Description

This invention relates to polymers of certain siloxanes and polyunsaturated hydrocarbons and a method for making them.

It has been known for quite some time that compounds containing the hydrosilane (i.e., $=\text{Si-H}$) functional group can be reacted with alkenes containing vinyl (terminal) unsaturation to form alkyl silanes. The simplest example of this reaction is the addition of trichlorosilane to ethylene to form ethyl trichlorosilane. This exothermic reaction is catalyzed by platinum halide compounds and proceeds readily to virtually 100% conversion.

This reaction, known as the "hydrosilation" or "hydrosilylation" reaction, has been found effective with a large number of vinyl compounds. Likewise, other silanes such as dialkyl silanes, halo-alkyl silanes, and alkoxy silanes have been found to undergo this reaction so long as they possess the requisite $=\text{Si-H}$ group.

A number of organosilicon polymers that have been disclosed in the prior art are actually vinyl addition polymers modified with silicon-containing moieties. Polymerization takes place in some cases via conventional olefin polymerization routes without making use of the hydrosilation reaction. The silicon containing moiety is then present as a polymer modifier. Examples of such polymerizations can be found in, e.g., U.S. 3,125,554; U.S. 3,375,236; U.S. 3,838,115; U.S. 3,920,714; and U.S. 3,929,850.

A few instances have been reported in which polymerization takes place via reaction between compounds containing a vinyl silane ($=\text{Si-CH=CH}_2$) group and a hydrosilane ($=\text{Si-H}$) group to form highly crosslinked, heat-set polymers. Examples of this type of polymer are found in U.S. Patent Nos. 3,197,432, 3,197,433 and 3,438,936. Each of these patents teaches the preparation of polymers from vinyl alkyl cyclotetrasiloxanes and alkyl cyclotetrasiloxanes containing 2 to 4 silanic hydrogen atoms.

Y.K. Kim et al. describe in the Journal of Polymer Science, Vol. 16 (1978), p. 483-490 a linear polycycloalkylene-siloxane polymer wherein the hydrocarbon rings are linked via $-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-$ groups but not via cyclic polysiloxanes or tetra(siloxy)silane residues as described below.

It would be desirable to provide a new class of high molecular weight organosilicon polymers which have excellent physical, thermal and electrical properties and outstanding resistance to water, and that could be used to prepare shaped articles.

According to the invention, a crosslinked or crosslinkable organosilicon polymer is characterized in that it comprises alternating polycyclic hydrocarbon residues and cyclic polysiloxanes or tetra(siloxy)silane residues linked through carbon to silicon bonds.

Preferably, the organosilicon polymer according to the invention is the reaction product of (a) a cyclic polysiloxane or a tetra(siloxy)silane containing at least two hydrosilane groups and (b) a polycyclic polyene, wherein the ratio of carbon-carbon double bonds in the rings of (b) to hydrosilane groups in (a) is greater than 0.5:1 and up to 1.8:1 and at least one of the hydrosilane groups of (a) or one of the carbon-carbon double bonds of the rings of (b) has more than two reactive sites.

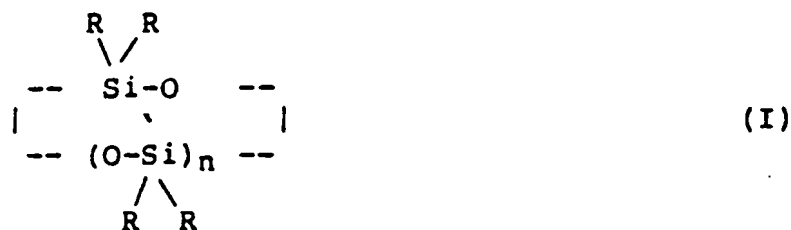
The term "hydrosilane groups" designates silicon bounded hydrogen atoms. The term "carbon-carbon double bonds" means non-aromatic carbon-carbon double bonds.

If thermoset polymers are desired, the ratio of carbon-carbon double bonds of (b) to hydrosilane groups in (a) is in the range of from 0.7:1 up to 1.3:1, more preferably from 0.8:1 up to 1.1:1. The alternating residues form a crosslinked thermoset structure.

If thermoplastic polymers are desired, the ratio of carbon-carbon double bonds in the rings of (b) to hydrosilation groups in (a) is greater than 0.5:1 and up to 0.7:1 or in the range of from 1.3:1 up to 1.8:1.

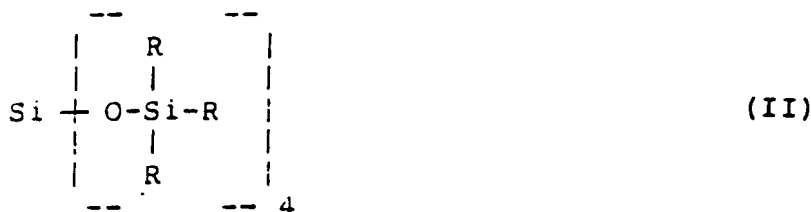
Also according to the invention, a method of preparing the organosilicon polymers according to the invention is characterized in that it comprises reacting, in the presence of a platinum-containing catalyst, (a) a cyclic or tetrahedral polysiloxane containing at least two hydrosilane groups and (b) a polycyclic polyene, the ratio of carbon-carbon double bonds in (b) to hydrosilane groups in the rings of (a) being greater than 0.5:1 and up to 1.8:1 and at least one of (a) and (b) having more than two reactive sites, and subjecting said polymer to heat to drive the crosslinking to a maximum.

Any cyclic polysiloxane or tetra(siloxy)silane with two or more hydrogen atoms bound to silicon will enter into the reaction. Cyclic polysiloxanes useful in forming the products of this invention have the general formula:



wherein R is hydrogen, a saturated, substituted or unsubstituted alkyl or alkoxy radical, a substituted or unsubstituted aromatic or aryloxy radical, n is an integer from 3 to 20, and R is hydrogen on at least two of the silicon atoms in the molecule.

The tetra(siloxy)silanes are represented by the general structural formula



wherein R is as defined above and is hydrogen on at least two of the silicon atoms in the molecule.

Examples of reactants of Formula (I) include, e.g., trimethyl cyclotrisiloxane, tetramethyl cyclotetrasiloxane, pentamethyl cyclopentasiloxane, hexamethyl cyclohexasiloxane, tetraethyl cyclotetrasiloxane, cyclotetrasiloxane, tetraphenyl cyclotetrasiloxane, tetraoctyl cyclotetrasiloxane and hexamethyl tetracyclosiloxane.

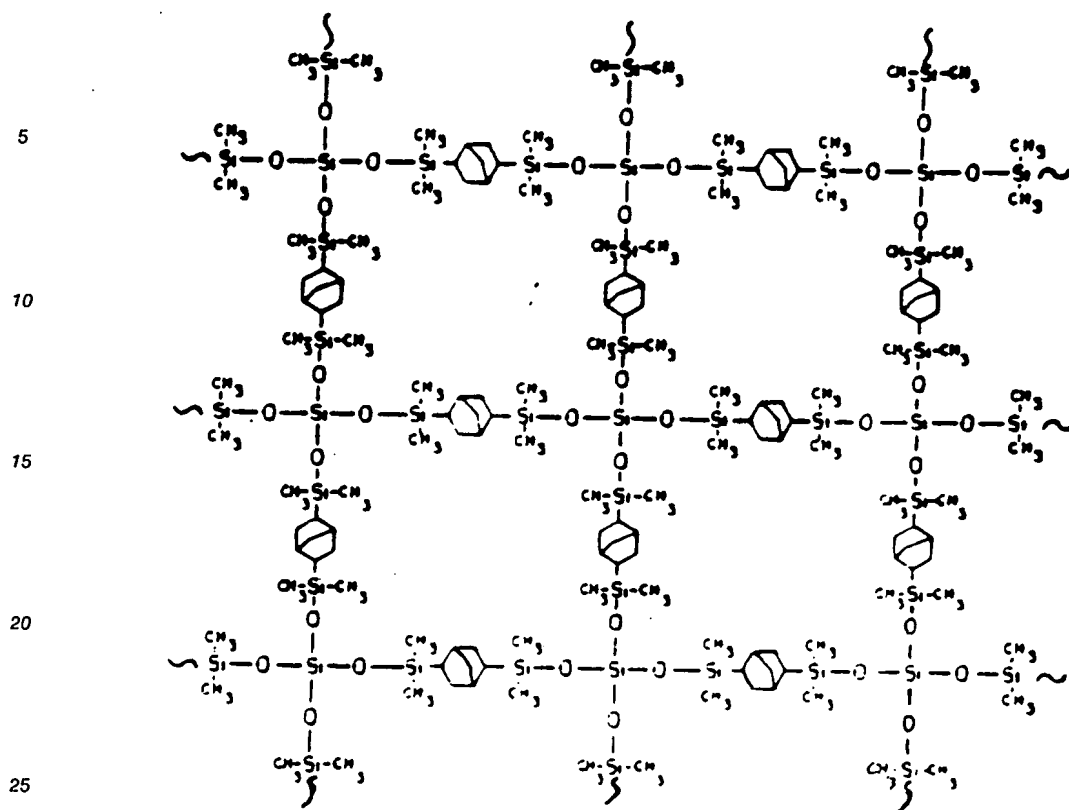
The most commonly occurring members of this group are the tetra-, penta-, and hexacyclosiloxanes, with tetramethyl tetracyclosiloxane being a preferred member. In most cases, however, the material is a mixture of a number of species wherein n can vary widely. Generally, commercial mixtures contain up to about 20% (in purer forms as low as 2%) low molecular weight linear methylhydrosiloxanes, such as heptamethyltrisiloxane, octamethyltrisiloxane, etc.

Examples of reactants of Formula (II) include, e.g., tetrakisdimethylsiloxysilane, tetrakisdiphenylsiloxysilane, and tetrakisdialkylsiloxysilane. The tetrakisdimethylsiloxysilane is the best known and preferred species in this group. Cyclic polyenes which can be employed are polycyclic hydrocarbon compounds having at least two non-aromatic carbon-carbon double bonds in their rings. Exemplary compounds include dicyclopentadiene, methyl dicyclopentadiene, cyclopentadiene oligomers, norbornadiene, norbornadiene dimer, hexahydronaphthalene, dimethanohexahydronaphthalene, and substituted derivatives of any of these.

The reaction proceeds readily in the presence of a platinum-containing catalyst. Metal salts and complexes of Group VIII elements can also be used. The preferred catalyst, in terms of both reactivity and cost, is chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$). Catalyst concentrations of 0.0005 to 0.5% by weight, based on weight of the monomer, will effect smooth and substantially complete polymerization. Other platinum compounds can also be used to advantage in some instances, such as PtCl_2 and dibenzonitrile platinum dichloride. Platinum on carbon is also effective for carrying out high temperature polymerizations. Other useful platinum catalysts are disclosed in, e.g., U.S. Patent Nos. 3,220,972, 3,715,334 and 3,159,662. An exhaustive discussion of the catalysis of hydrosilation can be found in *Advances in Organometallic Chemistry*, Vol. 17, beginning on page 407. The polymerization reactions can be promoted thermally or by the addition of radical generators such as peroxides and azo compounds.

It will be apparent to the artisan that the polymers of this invention can be homopolymers, i.e., reaction products of one hydrosilane-containing reactant and one polycyclic polyene, or they can be interpolymers prepared from a plurality of hydrosilane-containing reactants with one or more poly-cyclic polyenes. Any combination of silane-containing compound and polycyclic polyene is possible so long as the specified ratio of $>\text{C}=\text{C}<$ groups to $=\text{Si}-\text{H}$ groups is met.

One example of a crosslinked, thermoset polymer according to the invention is the reaction product of one mole of tetrakis dimethyl siloxysilane and 2 moles of norbornadiene which when fully cured, has the idealized general structural formula, for the 2,5 isomer (the 2,6 isomer can also be present):



It is possible, by selection of reactants, reactant concentrations and reaction conditions, to prepare polymers within the scope of this invention exhibiting a broad range of properties and physical forms. Thus, it has been found possible to prepare tacky solids, elastomeric materials, and tough glassy polymers.

The unique thermoset polymers of this invention have a range of utilities, depending upon their physical form. Tacky solids are useful as tackifiers in pressure sensitive adhesives and as contact adhesives. They are also useful as structural adhesives, curable in situ, to form strong bonds due to a high affinity of hydrosilane derived silanol groups for polar metal surfaces, especially oxidized metal surfaces. The elastomeric embodiments make excellent potting compounds for electronic applications since they can be cured in situ and are insensitive to water.

Thermal properties of these thermoset polymers are also outstanding. The glass transition temperature (T_g) of a fully cured thermoset polymer is 200°C or higher. Thermal stability is excellent with usually less than 10% weight loss at 500°C during thermogravimetric analysis. At 1100°C in air, they leave about 50% residue. The thermoset polymers are fire resistant and burn very slowly when subjected to a flame.

A particularly striking property of these thermoset polymers is their virtually total insensitivity to water. They have been found to be unaffected by boiling water after extended periods.

The thermoset polymers are also resistant to oxidation and to ultraviolet radiation at ordinary temperatures. Above 200°C , oxidative crosslinking of silicon portions of the molecule appears to take place, resulting in the formation of a dark siliceous outer layer. This oxidized outer layer appears to impede the oxidative degradation of the polymer.

The tough, glassy thermoset polymers may be useful in many applications where glass is now employed as, e.g., water heater tank liners. The insensitivity of these thermoset polymers to water and their high temperature properties make them ideal for applications of this type. Moreover, the impact resistance of glass fiber-filled polymer, although not extraordinary, is better than that of glass so that lined tanks can withstand the rigors of shipment, handling and installation better than glass.

The tough glassy thermoset polymers pyrolyze upon heating to greater than 1000°C . This high temperature resistance makes them useful as refractory materials, fire resistant materials and ablative materials.

The thermoplastic polymers of this invention generally exhibit melting points in the range of from 60°C to 130°C . However, when post-cured at temperatures greater than 200°C , some (for instance, those having a $>\text{C}=\text{C}=\text{Si}-\text{H}$ equivalents ratio of 1.45:1.0) exhibit elastomeric characteristics, and, in some instances, they have higher softening points or exhibit thermoset properties after post-cure.

The thermoplastic polymers of this invention range from tacky to hard, non-tacky solids which have low melting points. Some of the polymers (e.g., those having a $>C=C<=Si-H$ equivalents ratio of 1.45:1.0.) exhibit thermoplastic behavior (melt flow) until they are heated to a higher temperature (200 to 300°C) where they become thermoset polymers. These can be considered thermoplastic-thermoset polymers.

5 These materials can be coated on substrates as powders, melts, or solutions and cured to give glass transitions somewhat lower than the polymers that have mainly thermoset behavior (e.g., those having $>C=C<=Si-H$ equivalents ratio of 0.7:1 to 1.3:1).

To prepare the novel thermoset polymers of this invention, several approaches are available. In the first approach, the correct relative ratios of reactants and the platinum catalyst are simply mixed and brought to a temperature at which the reaction is initiated and proper temperature conditions are thereafter maintained to drive the reaction to substantial completion (typically, with a $>C=C<=Si-H$ equivalents ratio of 1:1, where 70 to 80% of the hydrosilane groups are consumed). Normally, periodic temperature increases are desirable to drive the reaction as the molecular weight of the polymer increases. The reaction is normally carried out in a mold, at least up until the point at which sufficient crosslinking has taken place to fix the polymer in the desired shape. Heat treatment can then be continued to drive the reaction further toward completion after removal from the mold, if necessary. This relatively simple approach is a workable method in cases where the two double bonds in the diene molecule are essentially equivalent in their reactivity so that crosslinking begins soon after initiation of the reaction.

Although a hydrosilation reaction via the carbon-carbon unsaturation of the polycyclic polyene rings and the hydrosilane group is the primary polymerization and crosslinking mechanism, other types of polymerization and crosslinking may also take place as the curing temperature is increased. These may include, e.g., oxidative crosslinking, free radical polymerization (olefin addition reactions) and condensation of silanols to form siloxane bonds.

The initial product of the reaction at lower temperatures is often a flowable, heat-curable liquid prepolymer or oligomer (hereafter "prepolymer") even though the ratio of $>C=C<$ to $=Si-H$ is otherwise suitable for crosslinking. Such liquid prepolymers, analogous to the so-called B-stage resins encountered in other thermoset preparations, can be recovered and subsequently transferred to a mold for curing. These viscous, flowable liquid prepolymers are stable at room temperature for varying periods of time, but, upon reheating to an appropriate temperature, they cure to the same types of thermoset polymers as are prepared when polymerization is carried out substantially immediately.

The B-stage type prepolymers can be prepared by cooling the reaction mass, following the initial exotherm, to 30 to 65°C and maintaining it at that point for several hours, and then interrupting the reaction by removing the heat until such time as it is desired to complete the transition to a glassy, crosslinked thermoset polymer. The viscous, flowable liquids will be 30 to 50% reacted and the viscosity can vary accordingly. By monitoring the viscosity build-up, the practitioner can select, for his own purposes, the point at which the polymerization is to be interrupted.

The thermoplastic polymers can be prepared in substantially the same manner as the thermoset polymers. That is, they may simply be prepared by mixing the correct ratios of reactants and catalyst and brought to the temperature at which the reaction is initiated. Thereafter, proper temperature conditions can be used to drive the reaction to completion. It is preferred for the temperature to be increased periodically as the molecular weight of the polymer increases.

The initial product of the reaction is a viscous, flowable liquid, which may be heated to complete polymerization, as described above. However, since the resultant polymers are thermoplastic, there is generally no need to retain the reactants in the form of a B stage prepolymer or oligomer such as those described above, as the polymer can be heated, molded and cooled to form a shaped article. Such thermoplastic polymers can be ground and shipped to a molder where they will be heated and formed into a shaped article. Thus, while liquid prepolymers, oligomers or polymer intermediates can be formed as described above, in most instances it will be preferable to prepare these thermoplastic polymers in the form of a solid, e.g., a powder, ready for use in a molding operation.

A number of options exist for incorporating additives into the polymer. Additives such as fillers and pigments are readily incorporated. Carbon black, vermiculite, mica, wollastonite, calcium carbonate, sand, glass spheres, glass beads, ground glass and waste glass are examples of fillers which can be incorporated. Fillers can serve either as reinforcement or as fillers and extenders to reduce the cost of the molded product. Glass spheres are useful for preparing low density composites. When used, fillers can be present in amounts up to about 80%. Stabilizers and antioxidants are useful to maintain storage stability of B stage materials and thermal oxidative stability of the final product.

Glass or carbon, e.g., graphite, fibers are wetted very well by the liquid prepolymer embodiment making the polymers excellent matrix materials for high strength composite structures. Thus a mold

containing the requisite staple or continuous filament can be charged with the prepolymer and the prepolymer cured to form the desired composite structure. Fiber in fabric form can also be employed. In addition, solid thermoplastic polymers may be melted, poured over such fibers, and heated to form composites or thermoplastic polymer powders may be blended with such fibers and, then, heated to form a composite. Fiber reinforced composites of the polymers of this invention can contain as much as 80%, preferably 30 to 60%, by weight, of fibrous reinforcement, and, when fully cured, typically exhibit extremely high tensile and flexural properties and also excellent impact strength. Other types of fibers, e.g., metallic, ceramic and synthetic polymer fibers, also work well.

The glass filled, thermoset products which have been polymerized to the tough glassy state are characterized by high physical properties, i.e., high modulus and high tensile strength and good flex properties. They are fire resistant, burn very slowly when subjected to a flame, and self-extinguish when the flame is removed.

The following examples are presented to demonstrate this invention. They are not intended to be limiting.

Example 1

This example shows preparation of a novel thermoset polymer per this invention by reacting dicyclopentadiene and tetrakisdimethylsiloxysilane, with a ratio of carbon-carbon double bonds to hydrosilane groups of 1:1.

A reaction vessel was dried using an N₂ flow and a heat gun (300 °C pot temperature), stoppered and placed in a nitrogen flushed glove bag while hot. After equilibrating, the reaction vessel was tared on a balance, returned to the glove bag, and 0.027 g of Pt Cl₂ was charged. A "dry" 1.27 cm (1/2") magnetic stirrer was charged and the reaction vessel was capped. Dicyclopentadiene (2.68 g; 0.02 mole) was charged to the reaction vessel using a 5cm³ syringe. This mixture was heated at 90 °C for 2 hours with stirring under slow N₂ purge to allow the catalyst complex to form. The sample was cooled to 35 °C, tetrakisdimethylsiloxysilane (3.28 g; 0.01 mole) was charged via syringe and the reaction mixture was returned to the 90 °C oil bath. After stirring for about 2 minutes, the sample foamed and darkened. The sample was further heated in the oil bath to 165 °C for 3 hours during which time polymerization occurred as the sample continued to thicken. Additional heat treatments of 190 °C for 1/2 hour, and 215 to 235 °C for 3 hours were performed. The sample was allowed to cool and removed from the reaction vessel. The final sample was dark, rubbery and tough.

Example 2

This example shows preparation of a film comprising a novel thermoset polymer per this invention, i.e., the reaction product of tetramethylcyclotetrasiloxane and norbornadiene, with a ratio of carbon-carbon double bonds to hydrosilane groups of 1:1.

Chloroplatinic acid (0.0030 g, 200 ppm) was charged to a reaction vessel under a nitrogen sweep. The reaction vessel was capped and 8.57 g (0.035 mole) tetramethylcyclotetrasiloxane and 6.43 g (0.070 mole) norbornadiene were charged to the sealed reaction vessel by syringe. The reaction vessel contents were blanketed under nitrogen and stirred while heating at 50 °C for 2.5 hours. After two hours the initial yellow color disappeared and the viscosity of the fluid increased. After the 2.5 hours at 50 °C the reaction mixture was diluted by injecting 15 ml dry xylene and filtered through #41 paper to remove insoluble black catalyst residues. The resulting polymer contained 10 to 50 ppm Pt (x-ray analysis).

Films of the filtered toluene solution 0.381mm (fifteen mils) thick were cast on glass plates with a doctor blade and the xylene was allowed to evaporate overnight. The films on the glass were heated at 100 °C for 70 hours under nitrogen and then at 200 °C for 4 hours. The films were immersed in water for a few hours at room temperature and they released from the glass. A visible/UV analysis showed no significant absorbance for these films from 220 to 800 nm.

Example 3

This example shows preparation of a molded, glass cloth reinforced, article comprising a novel thermoset polymer per this invention by preparing a B stage prepolymer by partially reacting dicyclopentadiene and tetramethylcyclotetrasiloxane (ratio of carbon-carbon double bonds to hydrosilane groups of 1:1), injecting the B stage prepolymer into a mold, and heating to complete polymerization.

Chloroplatinic acid (0.0101 g) was charged to a dry 750 ml reaction vessel in a N₂ filled glove bag and the reaction vessel was sealed. Dry dicyclopentadiene (26.44 g, 0.2 mole) was charged by syringe. This mixture was heated at 55 °C for one hour to form a dicyclopentadiene/H₂PtCl₆ • 6H₂O catalyst complex. Dry tetramethylcyclotetrasiloxane (24.05 g, 0.10 mole) was added gradually at 56 °C and an immediate exotherm took the temperature to 174 °C. The mixture was cooled to 64 to 65 °C and held there for 1.5 hour. Si²⁹NMR shows that the hydrosilation reaction is about 50% complete at this time. The low viscosity product was removed from the reaction vessel by syringe and injected into a teflon coated mold containing glass cloth which exactly filled the mold cavity. The resin in the mold was degassed at 60 °C under a slight vacuum in a vacuum oven. The aspirator vacuum was manually controlled to keep the resin from foaming out of the mold. The mold was heated in an oven at 68 °C for 18 hours and then at 140 to 150 °C for 3 days. The oven was cooled slowly and the mold unclamped to give a very hard, stiff 12.70 cm x 12.70 cm x 0.3175 cm (5" x 5" x 1/8") plaque. Samples were cut for rheological, tensile, and flexural property determinations and the following data were obtained:

60% Glass Cloth, 40% Tetramethylcyclotetrasiloxane/Dicyclopentadiene 1/2	
Tensile Strength	164101 KPa (23,800 psi)
Tensile Modulus	8.27x10 ⁶ KPa (1.2x10 ⁶ psi)
% Elongation (break)	2.2
Flexural Strength	278558 KPa (40,400 psi)
Flexural Modulus	1.57x10 ⁷ KPa (2.2x10 ⁶ psi)
Rockwell R Hardness	119
Glass Transition Temp (Rheometrics)	160 °C
Notched Izod Impact.	553.7 Jm ⁻¹ (10 ft lb/in notch)
Heat Distortion Temperature (1.82 MPa (264 psi))	>300 °C

Example 4

This example shows preparation of a novel thermoset polymer per this invention by reacting norbornadiene and tetramethylcyclotetrasiloxane with a ratio of carbon-carbon double bonds to hydrosilane groups of approximately 1:1.

A dry, N₂ sparged vessel was charged with a stir bar and 0.0021 g of H₂PtCl₆ • 6H₂O. The vessel was capped and charged with 4.47 g (0.05 mole) of norbornadiene. The resulting mixture was stirred for thirty minutes at 60 °C. Tetramethylcyclotetrasiloxane (5.83 g, 0.024 mole) was added and the reaction mixture gelled about three hours later. The sample was removed from the reaction vessel and cured at 150 °C for 16 hours, 250 °C for 2 hours and 280 °C for 16 hours to give a brown, glassy solid.

Example 5

This example shows preparation of a novel thermoset polymer per this invention by reacting dicyclopentadiene and methylcyclotetrasiloxane, with a ratio of carbon-carbon double bonds to hydrosilane groups of approximately 1:1.

Following the general procedure in Example 4, tetramethylcyclotetrasiloxane (18.1 g, 0.075 mole) was added to a heated (60 °C) mixture of dicyclopentadiene (20.12 g, 0.152 mole) and H₂PtCl₆ • 6H₂O (0.0076 g). The reaction mixture exothermed to 186 °C 30 seconds after the tetramethylcyclotetrasiloxane addition. The reaction mixture was stirred for 16 hours at 60 °C, 24 hours at 70 °C and 5 hours at 150 °C. The mixture was poured into an aluminum pan and cured for 12 hours at 200 °C, 2 hours at 225 °C, 2 hours at 250 °C and 16 hours at 280 °C to give a brown glassy solid.

The thermal stability of the polymers of Examples 4 and 5 are presented in the following table.

TGA (20 °C/Min.)		
Example No.	10% Wt. Loss (°C)	% Residue (1100 °C)
4	520	63
5	510	39

Example 6

This example shows preparation of a novel molded, thermoset polymer per this invention by reacting dicyclopentadiene and tetramethylcyclotetramethylsiloxane, with a ratio of carbon-carbon double bonds to hydrosilane groups of approximately 1:1.

Following the general procedure in Example 4, tetramethylcyclotetrasiloxane (49.76 g, 0.20 mole) was added to a heated (70 °C) mixture of dicyclopentadiene (54.71 g, 0.414 mole) and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.0209 g). Thirty seconds after the tetramethylcyclotetrasiloxane addition, the reaction mixture exothermed to 170 °C. The reaction mixture was stirred for 16 hours at 130 °C and poured into a teflon coated mold. The sample was cured for 16 hours at 150 °C to give an opaque, glassy solid.

Example 7

This example shows preparation of a molded, glass cloth reinforced, article comprising a novel thermoset polymer per this invention. A B stage prepolymer was prepared by partially reacting dicyclopentadiene and tetramethyl cyclotetrasiloxane in amounts such that the ratio of carbon-carbon double bonds to hydrosilane groups was 1.1:1. Then, the B stage prepolymer was poured into a mold containing a glass cloth and was heated to complete polymerization.

Following the general procedure in Example 4, tetramethylcyclotetrasiloxane (28.6 g, 0.12 mole) was added to a heated (55 °C) mixture of dicyclopentadiene (34.4 g, 0.26 mole) and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.0126 g). Thirty seconds after the tetramethyl cyclotetrasiloxane addition, the reaction mixture exothermed to 184 °C. The reaction mixture was stirred for 2 hours at 80 °C then transferred to a teflon-coated mold containing 50.9 g woven glass cloth. The sample was cured for 12 hours at 130 °C, for eight hours at 160 °C, and for 16 hours at 180 °C to give an opaque, glassy plaque containing 60.7 wt. % glass cloth. This plaque was further cured in a N_2 flushed oven at 200 °C, 250 °C and 310 °C for 4 hours at each temperature.

Example 8

This example shows preparation of a molded, opaque solid plaques comprising a novel thermoset polymer per this invention, by preparing a B stage prepolymer by partially reacting dicyclopentadiene and tetramethyl cyclotetrasiloxane (ratio of carbon-carbon double bonds to hydrosilane groups of 1:1), transferring the B stage prepolymer into a mold, and heating to complete polymerization.

Following the general procedure in Example 4, tetramethylcyclotetrasiloxane (76.36 g, 0.32 mole) was added to a heated (30 °C) mixture of dicyclopentadiene (83.9 g, 0.64 mole) and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.0148 g). Five minutes after this addition the reaction mixture exothermed to 193 °C. The reaction mixture was stirred for 1 hour at 55 to 70 °C, transferred to teflon-coated molds and cured at 145 °C for 18 hours under slight vacuum. The opaque solid plaques were further cured to 285 °C in a N_2 flushed oven.

The polymers of Examples 7 and 8 were further subjected to mechanical analysis to determine their glass transition temperature (T_g) and storage modulus (G') at various temperatures. Results are recorded in the following table.

Mechanical Analysis							
Example ⁽¹⁾	Wt. % Glass	T_g (°C)	G' (GPa) at T (°C)				
			25	100	140	180	200
7(a)	60.7	275	2.7	2.2	2.0	1.8	1.6
(b)	60.7	300	2.5	2.1	1.8	1.5	1.4
8(a)	0	245	0.8	0.57	0.50	0.43	0.35
(b)	0	250	0.78	0.60	0.50	0.40	0.35

(1) a Denotes data before water boil.

b Denotes data after 5 day water boil.

The data in this table demonstrate the relative water insensitivity of the organosilicon polymers of this invention. The weight gained after 5 days in boiling water was about 0.1%.

Example 9

This example shows preparation of a novel thermoset polymer per this invention by reacting a dicyclopentadieneoligomer comprising about 58.43% dicyclopentadiene, 43.75% tricyclopentadiene and 5.05% tetracyclopentadiene (analyzed by G.C.), and tetramethylcyclotetrasiloxane (ratio of carbon-carbon double bonds to hydrosilane groups of 0.86:1).

A complex of 0.0076 g of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 21.71 g (0.12 mole) of the dicyclopentadiene oligomer was prepared by heating the two materials under a dry nitrogen blanket for one hour at 50 °C. Tetramethylcyclotetrasiloxane (16.10 g, 0.07 mole) was added to the yellow complex (complex temperature was 71 °C). The reaction exothermed to 153 °C in 8 seconds. The yellow solution was cooled to 30 °C, poured into Teflon coated slotted molds and cured at 150 °C/16 hours and 200 °C/4 hours. The 1.27 cm x 7.62 cm x 0.32 cm (1/2"x3"x1/8") test pieces were removed from the mold and post cured at 100 °C/0.5 hours, 150 °C/0.5 hours, 200 °C/2 hours, 225 °C/2 hours, 250 °C/2 hours and 280 °C/16 hours.

The final polymer was a hard glassy solid with a glass transition temperature of 250 °C and the weight loss by thermogravimetric analysis started at 500 °C.

Example 10

This example shows the preparation of a molded article comprising a novel thermoset polymer per this invention, by partially reacting dicyclopentadiene and tetramethylcyclotetrasiloxane (ratio of carbon-carbon double bonds to hydrosilane groups of 1:1) to form a B stage type prepolymer, injecting the B stage prepolymer into a mold, and heating to complete polymerization.

The catalyst $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.0148 g) was charged to a dried 709 g (25 oz.) reaction vessel and sealed. Under a nitrogen blanket 83.95 g (0.635 mole) dicyclopentadiene was charged by syringe. The catalyst and dicyclopentadiene were heated for 90 minutes at 60 to 70 °C giving a yellow solution which was cooled to 30 °C. Tetramethylcyclotetrasiloxane (76.36 g, 0.317 mole) was added and an exothermic reaction started in two minutes, eventually reaching 193 °C. After cooling to 55 °C, a sample was injected into a 12.7 cm x 12.7 cm x 0.32 cm (5" x 5" x 1/8") teflon lined aluminium mold. The polymer was polymerized at temperatures ranging from 120 to 280 °C under a blanket of nitrogen. Some electrical properties of the cured polymer are given below:

Dielectric Constant	2.87 2.83	60 Hz 1 MHz
Dissipation Factor	0.0001 0.0002	60 Hz 100 KHz
Volume Resistivity ohm-cm	1.6 x 10 ¹⁸	
Dielectric Strength	15 MVm ⁻¹ (381 V/mil)	

A sample of the Example 10 polymer was immersed in boiling water for five days. The sample weight increased 0.1%. The dimensions of the sample (6.75, 1.30 cm, 0.32 cm) were unchanged after the boiling water treatment. The modulus/temperature curve and glass transition temperature (250 °C) were also unchanged by the boiling water treatment.

Example 11

This example shows preparation of a novel thermoset polymer per this invention by reacting dicyclopentadiene and a mixture of methylhydrocyclosiloxanes, with a ratio of carbon-carbon double bonds to hydrosilane groups of 0.7:1.

Chloroplatinic acid (0.0035g) was weighed into a 227g (8 oz.) reaction vessel under a nitrogen blanket in a dry box and the septum was sealed. Dry dicyclopentadiene (8.08g) was injected into the reaction vessel by a hypodermic syringe. The contents of the reaction vessel were heated to 60 to 65 °C for 1 hour, under a nitrogen blanket, and the chloroplatinic acid dissolved. Dry air was swept through the reaction vessel for 10 to 15 minutes and the contents were cooled to 31 °C. Methylhydrocyclosiloxanes, consisting of 54% tetramethyl cyclotetrasiloxane, 20% pentamethyl cyclopentasiloxane, 5% hexamethyl cyclohexasiloxane, 19% higher methylhydrocyclosiloxanes (up to approximately $(\text{CH}_3(\text{H})\text{SiO})_{20}$), and 2% linear methylhydrosiloxanes, (total 11.93g) were injected and the reaction exothermed to 179 °C. After cooling the

reaction product to 60 °C, it was poured into a teflon coated stainless steel mold. The mold was placed into a vacuum oven and a vacuum applied (approximately 1995 Pa (15 mm Hg) pressure, vacuum pump) for 10 to 15 minutes. Then, the mold was heated under nitrogen for 6 hours at 180 °C, for 6 hours at 225 °C, for 2 hours at 235 °C, and for 4 hours at 285 °C.

- 5 The polymer of this example exhibits thermoset behavior when polymerized at 225 °C. The polymer does not have a melting point, but softens at 100 °C to a soft extendable elastomer. The polymer is a tough, leather like solid at room temperature. It is flexible enough to be twisted 360 ° before tearing.

Example 12

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This example shows preparation of a novel thermoset polymer per this invention by reacting dicyclopentadiene and methylhydrocyclosiloxanes in the same manner as in example 11, except that the monomers were used in amounts such that the ratio of carbon-carbon double bonds to hydrosilane groups was 0.85:1 and the final heating was for 15 hours at 130 °C, for 6 hours at 160 °C, for 16 hours at 180 °C, 15 for 4 hours at 200 °C, and for 4 hours at 225 °C.

The thermoset polymer formed after heating to 225 °C was tougher than that from example 11. This hard, solid polymer maintains a high modulus up to 200 °C and exhibits elastomeric behavior when heated to 235 °C.

Example 13

- 20 This example shows preparation of a novel thermoset polymer per this invention by reacting dicyclopentadiene and methylhydrocyclosiloxanes in the same manner as in example 11, except that the monomers were used in amounts such that the ratio of carbon-carbon double bonds to hydrosilane groups 25 of 1.15:1 and the final heating was for 4 hours at 150 °C, for 2 hours at 235 °C, and for 4 hours at 285 °C.

Example 14

- 30 This example shows preparation of a novel thermoset polymer per this invention by reacting dicyclopentadiene and methylhydrocyclosiloxanes in the same manner as in example 13, except that the monomers were used in amounts such that the ratio of carbon-carbon double bonds to hydrosilane groups of 1.30:1.

- All the polymers produced in examples 12 to 14 exhibited thermoset characteristics and did not melt or lose their shape at temperatures below the decomposition points of the polymers (400 to 500 °C). Polymers 35 prepared from reactants having a carbon-carbon double bond:hydrosilane equivalents ratio near 1:1 were post-cured at 285 to 300 °C to increase their glass transition temperature to the 260 to 300 °C range. The cross-link density of such polymers was high enough to prevent segmental motion and network deformation.

Example 15

- This example shows preparation of a novel thermoset polymer per this invention by reacting dicyclopentadiene and methylhydrocyclosiloxanes in the same manner as in example 11, except that the monomers were used in amounts such that the ratio of carbon-carbon double bonds to hydrosilane groups 45 was 1.46:1 and the final heating was for 6 hours at 150 °C, for 6 hours at 200 °C, for 2 hours at 235 °C, and for 4 hours at 285 °C.

- Example 15 demonstrates polymerization in the transition range from thermoset behavior to thermoplastic behavior. When polymerized up to 200 °C, the sample softened to a highly compressible elastomer at about 120 to 125 °C. When the sample was post-cured at 285 °C, the glass transition temperature was 50 raised to only 200 °C. The degree of crosslinking was limited by available hydrosilane groups.

Example 16

- This example shows preparation of a novel thermoplastic polymer per this invention by reacting 55 dicyclopentadiene and methylhydrocyclosiloxanes in the same manner as in example 11, except in amounts such that the ratio of carbon-carbon double bonds to hydrosilane groups was 1.61:1 and the final heating was for 6 hours at 150 °C, for 6 hours at 200 °C, for 8 hours at 235 °C, and for 4 hours at 285 °C.

Example 17

This example shows preparation of a novel thermoplastic polymer per this invention by reacting dicyclopentadiene and methylhydrocyclosiloxanes in amounts such that the ratio of carbon-carbon double bonds to hydrosilane groups was 1.75:1.

A catalyst solution containing 600 ppm chloroplatinic acid was prepared by heating 0.0953g of chloroplatinic acid with 158.8g dicyclopentadiene to 70 °C for 1.5 hours in a sealed 227g (8 ounce) reaction vessel, under nitrogen. A 150 ppm chloroplatinic acid solution was prepared by diluting 30g of the above catalyst solution with 90g of dicyclopentadiene. A portion of the resultant chloroplatinic acid solution (7.92g) was weighed into a 17.7 cm (7 inch) reaction vessel with 4.59g of dicyclopentadiene, making a 95 ppm concentration of chloroplatinic acid in dicyclopentadiene (0.185 gram equivalent of olefin). Then, 7.21 g (0.106 hydrosilane equivalents) of methylsiloxanes (described in example 11) were injected into the sealed reaction vessel at 23 °C. The reaction mixture was heated to 36 °C and a slight exotherm raised the temperature to 60 °C, where the mixture became viscous. A vacuum 1995 Pa (15 mm Hg) was applied to the contents of the reaction vessel at 45 °C for 10 minutes to pull gas out of the reaction product. The product was poured into a teflon coated stainless steel mold and heated in a nitrogen blanket for 6 hours at 150 °C, for 20 hours at 200 °C, and for 6 hours at 225 to 235 °C. The 7.62 cm x 1.27 cm x 0.32 cm (3"x1/2"x1/8") specimens removed from the mold were transparent, hard solid with a melting point of 117 to 125 °C. This solid could be ground into a crystalline powder.

The polymers of examples 16 and 17 do not form a complete polymeric network, even when they are polymerized at 225 to 235 °C. They are completely thermoplastic and form a viscous, flowable liquid above their melting points. The solids can be ground into powder.

The properties of the polymers prepared in examples 11 to 17 are shown in the following Table.

		Organosilicon Polymers (Examples 11 to 17) Dicyclopentadiene/Methylhydrocyclopentadiene					
		Example No.					
		11	12	13	14	15	16
5	>C=C<:Si-H Equiv. Ratio	0.70	0.85	1.15	1.30	1.46	1.61
	Chloroplatinic Acid Catalyst (ppm) ^a	175	174	178	177	179	181
	Max. Polymerization Temp. (°C)	225 (285)	225	150	150 (285)	200 (285)	235
10	MP100 Melting/Softening Point	SP100	300	300	300	SP120-125	MP120-125
	Glass Transition Temp. (°C)	100	235	155	135 (210)	120 (200)	-
	Mechanical Thermal DSC ^{ee}	-	-	-	108	88	-
15	Initial Weight Loss TGA, °C. (8 residue, 1000°C)	-	-	-	460 (43.5)	470 (33.7)	450 (44.1)
	M _n Air	-	-	-	470 (35.6)	450 (33.7)	450 (33.6)
		-	-	-	500 (47.0)	500 (33.4)	500 (33.4)

^a Calculated by dividing the total weight of the dry chloroplatinic acid by the total weight of all the reactants.

^{ee} Differential Scanning Calorimeter.

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Example 18

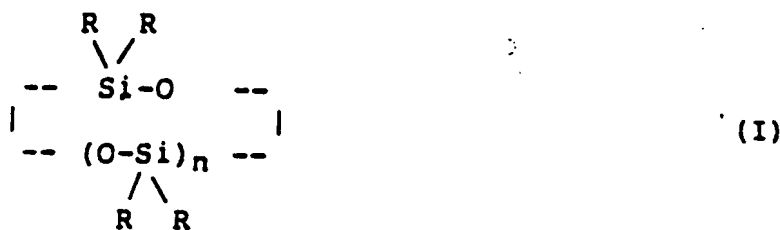
This example shows preparation of graphite fiber composite.

- Chloroplatinic acid (0.0185g) was weighed into a reaction vessel in a dry box and the reaction vessel was sealed. Dicyclopentadiene (47.15g, 0.357 mole, 0.714 equivalents) was injected into the reaction vessel and the mixture was heated with stirring to 60°C for 1 hour. After cooling to 36°C, tetramethylcyclotetrasiloxane (44.67g) was injected. In two minutes, the sample exothermed to 192°C. The product was cooled and injected into a teflon lined mold 12.7 cm x 12.7 cm x 0.32 cm (5" x 5" x 1/8") containing ten 12.7 cm x 12.7 cm (5" x 5") sheets of square woven graphite fiber cloth. The loaded mold was heated in a nitrogen blanketed oven for 15 hours at 130°C, for 6 hours at 160°C, and for 12 hours at 180°C. The resulting composite had good flexural strength 468860 KPa (68,000 psi) and modulus 3.24×10^7 KPa (4.7×10^6 psi).

Claims

- Claims for the following Contracting States : DE, GB, FR, IT, NL, SE, BE**

1. A crosslinked or crosslinkable organosilicon polymer is characterized in that it comprises alternating (1) polycyclic hydrocarbon residues and (2) cyclic polysiloxanes or tetra(siloxy)silane residues linked through carbon to silicon bonds.
2. A crosslinked or crosslinkable organosilicon polymer according to claim 1, which is the reaction product of
 - (a) a silicon-containing reactant selected from a cyclic polysiloxane, a tetra(siloxy)silane and mixtures of one of these, said reactant having as reactive sites at least two hydrogen atoms per molecule bonded directly to silicon and
 - (b) a polycyclic polyene, containing as reactive sites at least two non-aromatic carbon-carbon double bonds in the rings per molecule, wherein the ratio of said carbon-carbon double bonds in (b) to said silicon-bonded hydrogen atoms in (a) is greater than 0.5:1 and up to 1.8:1 and at least one of the reactants (a) or (b) has more than two of said reactive sites per molecule.
3. A polymer as claimed in claim 2, further characterized in that the silicon-containing reactant is:

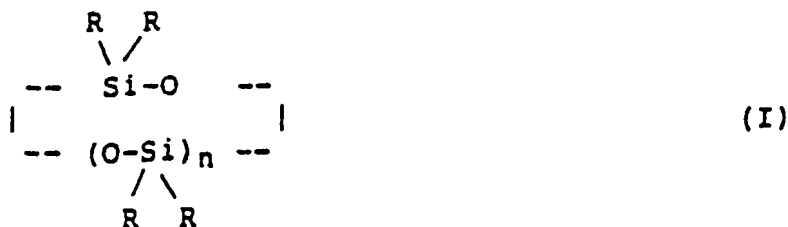


wherein R, which can be the same or different, is hydrogen, a saturated, substituted or unsubstituted alkyl or alkoxy radical, a substituted or unsubstituted aromatic or aryloxy radical, n is an integer from 3 to 20, and R is hydrogen on at least two of the silicon atoms in the molecule; or is:



wherein R is as defined above and is hydrogen on at least two silicon atoms in the molecule.

4. A crosslinked or crosslinkable organosilicon polymer as claimed in claim 2, further characterized in that the polycyclic polyene is norbornadiene, dicyclopentadiene, tricyclopentadiene, hexahydronaphthalene dimethanohexahydronaphthalene, or norbornadiene dimer.
5. A crosslinked organosilicon polymer as claimed in any of the claims 1-4, further characterized in that the ratio of carbon-carbon double bonds in the rings of (b) to silicon-bonded hydrogen atoms in (a) is in the range of from 0.7:1 up to 1.3:1, and the alternating residues form a crosslinked thermoset structure.
6. A crosslinked organosilicon polymer as claimed in claim 5, further characterized in that the ratio of carbon-carbon double bonds in the rings of (b) to silicon-bonded hydrogen atoms in (a) is in the range of from 0.8:1 up to 1.1:1.
7. A crosslinkable organosilicon polymer as claimed in any of claims 1-6, further characterized in that it is thermoplastic and the ratio of carbon-carbon double bonds in the rings of (b) to silicon-bonded hydrogen atoms in (a) is greater than 0.5:1 and up to 0.7:1, or in the range of from 1.3:1 up to 1.8:1.
8. Use of the organosilicon polymer of any of the preceding claims in a fiber reinforced composite structure comprising up to 80%, by weight of a fibrous reinforcement.
9. Use as claimed in claim 8 of the organosilicon polymer, further characterized in that the fibrous reinforcement is glass, carbon, metallic, ceramic, or synthetic polymer fibers, or a fiber mat.
10. A method for preparing the organosilicon polymers as claimed in claims 1 to 9, characterized in that it comprises reacting, in the presence of a platinum-containing catalyst, (a) a cyclic polysiloxane or tetra(siloxy)silane containing as reactive sites at least two silicon-bonded hydrogen atoms and (b) a polycyclic polyene, containing as reactive sites at least two non-aromatic carbon-carbon double bonds in the rings per molecule, the ratio of carbon-carbon double bonds in the rings of (b) to silicon bonded hydrogen atoms in (a) being greater than 0.5:1 and up to 1.8:1 and at least one of the reactants (a) or (b) having more than two reactive sites, and subjecting said polymer to heat to drive the crosslinking to a maximum.
11. A method for preparing organosilicon polymers as claimed in claim 10, further characterized in that the cyclic polysiloxane is:



wherein R is hydrogen, a saturated, substituted or unsubstituted alkyl or alkoxy radical, a substituted or unsubstituted aromatic or aryloxy radical, n is an integer from 3 to 20, and R is hydrogen on at least two of the silicon atoms in the molecule; or the tetra(siloxy)silane is:



wherein R is as defined above and is hydrogen at at least two silicon atoms in the molecule.

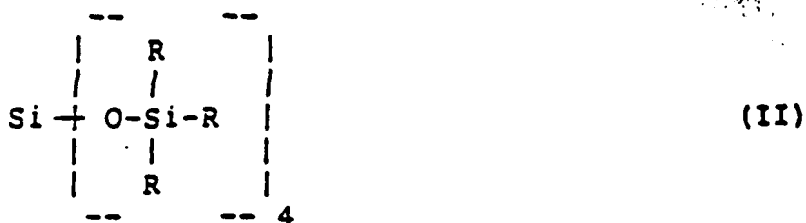
12. A method for preparing organosilicon polymers as claimed in claim 10, further characterized in that the ratio of carbon-carbon double bonds in the rings of (b) to silicon-bonded hydrogen atoms in (a) is in the range of 0.7:1 up to 1.3:1.
13. A method for preparing organosilicon polymers as claimed in claim 12, further characterized in that the ratio of carbon-carbon double bonds in the rings of (b) to silicon-bonded hydrogen atoms in (a) is in the range of from 0.8:1 up to 1.1:1.
14. A method for preparing organosilicon polymers as claimed in any of claims 10 to 13, further characterized in that the platinum-containing catalyst is selected from chloroplatinic acid, PtCl_2 and dibenzonitrile platinum dichloride.
15. A method for preparing organosilicon polymers as claimed in any of claims 10 to 14, further characterized in that it includes the steps of: (i) partially reacting (a) and (b) to form a prepolymer; (ii) transferring the prepolymer to a mold; and (iii) curing the prepolymer to form a molded thermoset product.

Claims for the following Contracting State : ES

1. A method for preparing a crosslinked or crosslinkable organosilicon polymer comprising alternating (1) polycyclic hydrocarbon residues and (2) cyclic polysiloxanes or tetra(siloxy)silane residues linked through carbon to silicon bonds, characterized in that it comprises reacting, in the presence of a platinum-containing catalyst, (a) a cyclic polysiloxane or tetra(siloxy)silane containing as reactive sites at least two silicon-bonded hydrogen atoms and (b) a polycyclic polyene, containing as reactive sites at least two non-aromatic carbon-carbon double bonds in the rings per molecule, the ratio of carbon-carbon double bonds in (b) to silicon-bonded hydrogen atoms in the rings of (a) being greater than 0.5:1 and up to 1.8:1 and at least one of the reactants (a) or (b) having more than two reactive sites, and subjecting said polymer to heat to drive the crosslinking to a maximum.
2. A method for preparing organosilicon polymers as claimed in claim 1, further characterized in that the cyclic polysiloxane is:



wherein R is hydrogen, a saturated, substituted or unsubstituted alkyl or alkoxy radical, a substituted or unsubstituted aromatic or aryloxy radical, n is an integer from 3 to 20, and R is hydrogen on at least two of the silicon atoms in the molecule; or the tetra(siloxy)silane is:



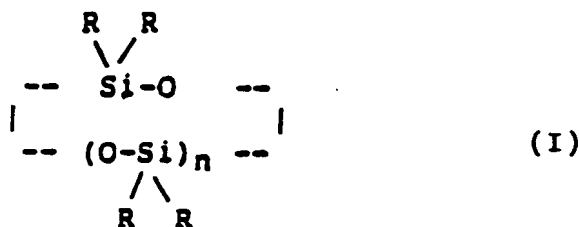
wherein R is as defined above and is hydrogen at at least two silicon atoms in the molecule.

3. A method for preparing organosilicon polymers as claimed in claim 1, further characterized in that the ratio of carbon-carbon double bonds in the rings of (b) to silicon-bonded hydrogen atoms in (a) is in the range of 0.7:1 up to 1.3:1.
- 5 4. A method for preparing organosilicon polymers as claimed in claim 3, further characterized in that the ratio of carbon-carbon double bonds in the rings of (b) to silicon-bonded hydrogen atoms in (a) is in the range of from 0.8:1 up to 1.1:1.
- 10 5. A method for preparing organosilicon polymers as claimed in any of claims 1 to 4, further characterized in that the platinum-containing catalyst is selected from chloroplatinic acid, PtCl_2 and dibenzonitrile platinum dichloride.
- 15 6. A method for preparing organosilicon polymers as claimed in any of claims 1 to 5, further characterized in that it includes the steps of: (i) partially reacting (a) and (b) to form a prepolymer; (ii) transferring the prepolymer to a mold; and (iii) curing the prepolymer to form a molded thermoset product.
- 20 7. Method for preparing organosilicon polymers as claimed in any of claims 1 to 6, further characterized in that the polycyclic polyene is norbornadiene, dicyclopentadiene, tricyclopentadiene, hexahydronaphthalene, dimethanohexahydronaphthalene, or norbornadiene dimer.
8. Use of the organosilicon polymer of any of the preceding claims in a fiber reinforced composite structure comprising up to 80%, by weight of a fibrous reinforcement.
- 25 9. Use as claimed in claim 8 of the organosilicon polymer, further characterized in that the fibrous reinforcement is glass, carbon, metallic, ceramic, or synthetic polymer fibers, or a fiber mat.

Patentansprüche

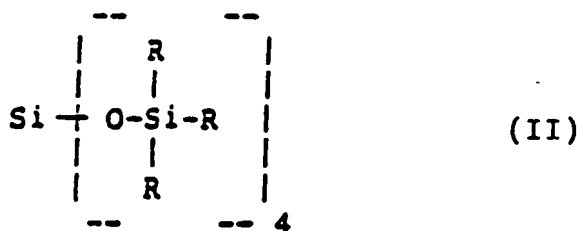
Patentansprüche für folgende Vertragsstaaten : DE, GB, FR, IT, NL, SE, BE

- 30 1. Quervernetztes oder quervernetzbares Organosiliciumpolymer, dadurch gekennzeichnet, daß es alternierend (1) polycyclische Kohlenwasserstoffreste und (2) cyclische Polysiloxane oder Tetra(siloxy)silanreste umfaßt, die über Kohlenstoff-Silicium-Bindungen verbunden sind.
- 35 2. Quervernetztes oder quervernetzbares Organosiliciumpolymer nach Anspruch 1, das das Reaktionsprodukt ist aus
 - (a) einem siliciumhaltigen Reaktanten ausgewählt aus einem cyclischen Polysiloxan, einem Tetra(siloxy)silan und Mischungen von einem der beiden, wobei besagter Reaktant als Reaktionsstellen mindestens zwei Wasserstoffatome pro Molekül aufweist, die direkt an Silicium gebunden sind und
 - (b) einem polycyclischen Polyen, das als Reaktionsstellen mindestens zwei nichtaromatische Kohlenstoff-Kohlenstoff-Doppelbindungen in den Ringen pro Molekül enthält,
 - 40 worin das Verhältnis der besagten Kohlenstoff-Kohlenstoff-Doppelbindungen in (b) zu besagten, an Silicium gebundenen Wasserstoffatomen in (a) größer als 0,5:1 und bis 1,8:1 ist und mindestens einer der Reaktanten (a) oder (b) mehr als zwei besagte Reaktionsstellen pro Molekül aufweist.
- 45 3. Polymer nach Anspruch 2, weiterhin dadurch gekennzeichnet, daß der siliciumhaltige Reaktant ist:



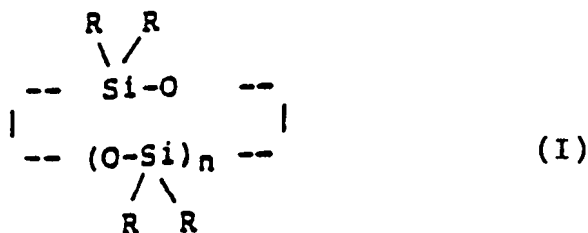
worin R, das gleich oder verschieden sein kann, Wasserstoff, ein gesättigter, substituierter oder

unsubstituierter Alkyl- oder Alkoxyrest, ein substituierter oder unsubstituierter aromatischer Rest oder Aryloxyrest ist, n eine ganze Zahl zwischen 3 und 20 ist, und R an mindestens zwei Siliciumatomen im Molekül Wasserstoff ist, oder:

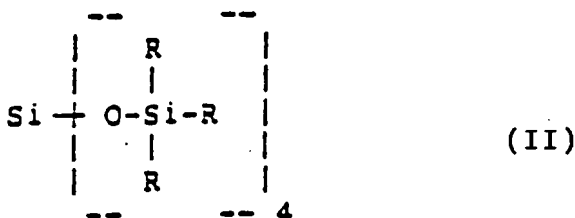


worin R wie oben definiert ist und an mindestens zwei Siliciumatomen im Molekül Wasserstoff ist.

4. Quervernetztes oder quervernetzbares Organosiliciumpolymer nach Anspruch 2, weiterhin dadurch gekennzeichnet, daß das polycyclische Polyen Norbornadien, Dicyclopentadien, Tricyclopentadien, Hexahydronaphthalin, Dimethanohexahydronaphthalin oder Norbornadiendimer ist.
5. Quervernetztes Organosiliciumpolymer nach einem der Ansprüche 1 bis 4, weiterhin dadurch gekennzeichnet, daß das Verhältnis der Kohlenstoff-Kohlenstoff-Doppelbindungen in den Ringen von (b) zu den an Silicium gebundenen Wasserstoffatomen in (a) im Bereich von 0,7:1 bis 1,3:1 liegt, und die alternierenden Reste eine quervernetzte Duroplast-Struktur bilden.
6. Quervernetztes Organosiliciumpolymer nach Anspruch 5, weiterhin dadurch gekennzeichnet, daß das Verhältnis der Kohlenstoff-Kohlenstoff-Doppelbindungen in den Ringen von (b) zu den an Silicium gebundenen Wasserstoffatomen in (a) im Bereich von 0,8:1 bis 1,1:1 liegt.
7. Quervernetzbares Organosiliciumpolymer nach einem der Ansprüche 1 bis 6, weiterhin dadurch gekennzeichnet, daß es thermoplastisch ist und das Verhältnis der Kohlenstoff-Kohlenstoff-Doppelbindungen in den Ringen von (b) zu den an Silicium gebundenen Wasserstoffatomen in (a) größer als 0,5:1 und bis 0,7:1 ist oder im Bereich von 1,3:1 bis 1,8:1 liegt.
8. Verwendung des Organosiliciumpolymers nach einem der vorhergehenden Ansprüche in einer faserverstärkten Verbundkonstruktion umfassend bis zu 80 Gewichts-% einer Faserverstärkung.
9. Verwendung nach Anspruch 8 des Organosiliciumpolymers, weiterhin dadurch gekennzeichnet, daß die Faserverstärkung aus Glas-, Kohlenstoff-, Metall-, Keramik- oder synthetischen Polymerfasern besteht oder eine Fasermatte ist.
10. Verfahren zur Herstellung der Organosiliciumpolymere nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß es umfaßt: Umsetzen, in Gegenwart eines platinhaltigen Katalysators, eines (a) cyclischen Polysiloxans oder Tetra(siloxy)silans enthaltend als reaktive Stellen mindestens zwei an Silicium gebundene Wasserstoffatome und (b) ein polycyclisches Polyen enthaltend als reaktive Stellen mindestens zwei nichtaromatische Kohlenstoff-Kohlenstoff-Doppelbindungen in den Ringen pro Molekül, wobei das Verhältnis der Kohlenstoff-Kohlenstoff-Doppelbindungen in den Ringen von (b) zu den an Silicium gebundenen Wasserstoffatomen in (a) größer als 0,5:1 und bis 1,8:1 ist und mindestens einer der Reaktanten (a) oder (b) mehr als zwei reaktive Stellen hat, und Wärmeaussetzung des besagten Polymers, um die Quervernetzung zum Maximum zu bringen.
11. Verfahren zur Herstellung von Organosiliciumpolymeren nach Anspruch 10, weiterhin dadurch gekennzeichnet, daß das cyclische Polysiloxan ist:



worin R Wasserstoff, ein gesättigter, substituierter oder unsubstituierter Alkyl- oder Alkoxyrest, ein substituierter oder unsubstituierter aromatischer Rest oder Aryloxyrest ist, n eine ganze Zahl zwischen 3 und 20 ist, und R an mindestens zwei Siliciumatomen im Molekül Wasserstoff ist; oder das Tetra(siloxy)silan ist:



worin R wie oben definiert ist und an mindestens zwei Siliciumatomen im Molekül Wasserstoff ist.

12. Verfahren zur Herstellung von Organosilicumpolymeren nach Anspruch 10, weiterhin dadurch gekennzeichnet, daß das Verhältnis der Kohlenstoff-Kohlenstoff-Doppelbindungen in den Ringen von (b) zu den an Silicium gebundenen Wasserstoffatomen in (a) im Bereich von 0,7:1 bis 1,3:1 liegt.

13. Verfahren zur Herstellung von Organosilicumpolymeren nach Anspruch 12, weiterhin dadurch gekennzeichnet, daß das Verhältnis der Kohlenstoff-Kohlenstoff-Doppelbindungen in den Ringen von (b) zu den an Silicium gebundenen Wasserstoffatomen in (a) im Bereich von 0,8:1 bis 1,1:1 liegt.

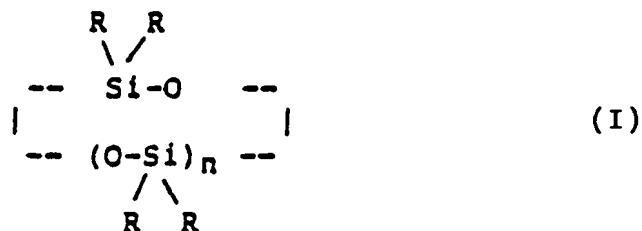
14. Verfahren zur Herstellung von Organosilicumpolymeren nach einem der Ansprüche 10 bis 13, weiterhin dadurch gekennzeichnet, daß der platinhaltige Katalysator ausgewählt ist aus Chlorplatinsäure, PtCl_2 und Dibenzonitrilplatindichlorid.

15. Verfahren zur Herstellung von Organosilicumpolymeren nach einem der Ansprüche 10 bis 14, weiterhin dadurch gekennzeichnet, daß es die folgenden Schritte umfaßt: (i) teilweises Umsetzen von (a) und (b) zur Bildung eines Prepolymers; (ii) Übertragung des Prepolymers in eine Gußform; und (iii) Härten des Prepolymers zur Bildung eines geformten duroplastischen Produkts.

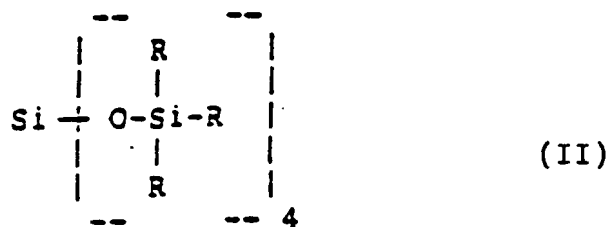
Patentansprüche für folgenden Vertragsstaat : ES

1. Verfahren zur Herstellung eines quervernetzten oder quervernetzbaaren Organosilicumpolymers umfassend alternierend (1) polycyclische Kohlenwasserstoffreste und (2) cyclische Polysiloxane oder Tetra(siloxy)silanreste, die über Kohlenstoff-Silicium-Bindungen verbunden sind, dadurch gekennzeichnet, daß es das Umsetzen, in Gegenwart eines platinhaltigen Katalysators, (a) eines cyclischen Polysiloxans oder Tetra(siloxy)silans, enthaltend als reaktive Stellen mindestens zwei an Silicium gebundene Wasserstoffatome, und (b) ein polycyclisches Polyen, enthaltend als reaktive Stellen mindestens zwei nichtaromatische Kohlenstoff-Kohlenstoff-Doppelbindungen in den Ringen pro Molekül, umfaßt, wobei das Verhältnis der Kohlenstoff-Kohlenstoff-Doppelbindungen in (b) zu den an Silicium gebundenen Wasserstoffatomen in den Ringen von (a) größer als 0,5:1 und bis 1,8:1 ist und mindestens einer der Reaktanten (a) oder (b) mehr als zwei reaktive Stellen hat, und Wärmeaussetzung des besagten Polymers, um die Quervernetzung zum Maximum zu bringen.

2. Verfahren zur Herstellung von Organosiliciumpolymeren nach Anspruch 1, weiterhin dadurch gekennzeichnet, daß das cyclische Polysiloxan ist:



worin R Wasserstoff, ein gesättigter, substituierter oder unsubstituierter Alkyl- oder Alkoxyrest, ein substituierter oder unsubstituierter aromatischer Rest oder Aryloxyrest ist, n eine ganze Zahl zwischen 3 und 20 ist, und R an mindestens zwei Siliciumatomen im Molekül Wasserstoff ist; oder das Tetra(siloxy)silan ist:



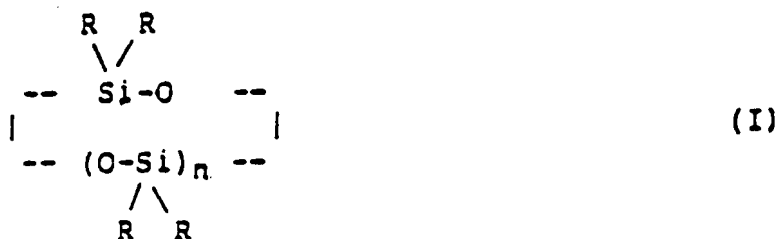
worin R wie oben definiert ist und an mindestens zwei Siliciumatomen im Molekül Wasserstoff ist.

3. Verfahren zur Herstellung von Organosiliciumpolymeren nach Anspruch 1, weiterhin dadurch gekennzeichnet, daß das Verhältnis der Kohlenstoff-Kohlenstoff-Doppelbindungen in den Ringen von (b) zu den an Silicium gebundenen Wasserstoffatomen in (a) im Bereich von 0,7:1 bis 1,3:1 liegt.
4. Verfahren zur Herstellung von Organosiliciumpolymeren nach Anspruch 3, weiterhin dadurch gekennzeichnet, daß das Verhältnis der Kohlenstoff-Kohlenstoff-Doppelbindungen in den Ringen von (b) zu den an Silicium gebundenen Wasserstoffatomen in (a) im Bereich von 0,8:1 bis 1,1:1 liegt.
5. Verfahren zur Herstellung von Organosiliciumpolymeren nach einem der Ansprüche 1 bis 4, weiterhin dadurch gekennzeichnet, daß der platinhaltige Katalysator ausgewählt ist aus Chlorplatinsäure, PtCl_2 und Dibenzonitrilplatindichlorid.
6. Verfahren zur Herstellung von Organosiliciumpolymeren nach einem der Ansprüche 1 bis 5, weiterhin dadurch gekennzeichnet, daß es die folgenden Schritte umfaßt: (i) teilweises Umsetzen von (a) und (b) zur Bildung eines Prepolymers; (ii) Übertragung des Prepolymers in eine Gußform; und (iii) Härten des Prepolymers zur Bildung eines geformten duroplastischen Produkts.
7. Verfahren zur Herstellung von Organosiliciumpolymeren nach einem der Ansprüche 1 bis 6, weiterhin dadurch gekennzeichnet, daß das polycyclische Polyen Norbornadien, Dicyclopentadien, Tricyclopentadien, Hexahydronaphthalin, Dimethanohexahydronaphthalin oder Norbornadiendimer ist.
8. Verwendung des Organosiliciumpolymers nach einem der vorhergehenden Ansprüche in einer faserverstärkten Verbundkonstruktion umfassend bis zu 80 Gewichts-% einer Faserverstärkung.
9. Verwendung nach Anspruch 8 des Organosiliciumpolymers, weiterhin dadurch gekennzeichnet, daß die Faserverstärkung aus Glas-, Kohlenstoff-, Metall-, Keramik- oder synthetischen Polymerfasern besteht oder eine Fasermatte ist.

Revendications

Revendications pour les Etats contractants suivants : DE, GB, FR, IT, NL, SE, BE

1. Polymère organosilicié réticulé ou réticulable, caractérisé en ce qu'il comprend en alternance (1) des restes hydrocarbonés polycycliques et (2) des restes polysiloxane cycliques ou tétra(siloxy)silane reliés par des liaisons carbone-silicium.
2. Polymère organosilicié réticulé ou réticulable selon la revendication 1, qui est le produit de la réaction de
 - (a) un réactif contenant du silicium choisi parmi un polysiloxane cyclique, un tétra(siloxy)silane et des mélanges de l'un de ceux-ci, ledit réactif comportant comme sites réactifs au moins deux atomes d'hydrogène par molécule reliés directement au silicium et
 - (b) un polyène polycyclique contenant comme sites réactifs au moins deux doubles liaisons carbone-carbone non aromatiques dans les cycles, par molécule,
 dans lequel le rapport desdites doubles liaisons carbone-carbone dans (b) auxdits atomes d'hydrogène liés au silicium dans (a) est supérieur à 0,5:1, pouvant atteindre une valeur de 1,8:1 et au moins l'un des réactifs (a) ou (b) comporte plus de deux desdits sites réactifs par molécule.
3. Polymère selon la revendication 2, caractérisé en ce que le réactif contenant du silicium est :



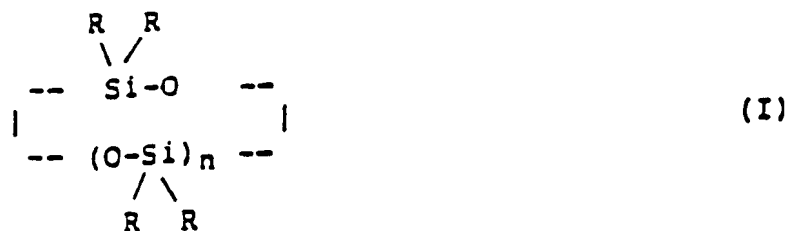
dans laquelle les radicaux R, qui peuvent être identiques ou différents, représentent un atome d'hydrogène, un radical alkyle ou alcoxy saturé, substitué ou non substitué, un radical aromatique ou aryloxy substitué ou non substitué, n est un nombre entier compris entre 3 et 20, et R est un atome d'hydrogène sur au moins deux des atomes de silicium dans la molécule; ou est :



dans laquelle R est tel que défini ci-dessus et est un atome d'hydrogène sur au moins deux atomes de silicium dans la molécule.

4. Polymère organosilicié réticulé ou réticulable selon la revendication 2, caractérisé en ce que le polyène polycyclique est le norbornadiène, le dicyclopentadiène, le tricyclopentadiène, l'hexahydronaphtalène, le diméthanoexahydronaphtalène, ou le norbornadiène dimère.
5. Polymère organosilicié réticulé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que le rapport des doubles liaisons carbone-carbone dans les cycles de (b) aux atomes d'hydrogène liés au silicium dans (a) est compris entre 0,7:1 et 1,3:1, et les restes en alternance forment une structure thermodurcissable réticulée.

6. Polymère organosilicié réticulé selon la revendication 5, caractérisé en ce que le rapport des doubles liaisons carbone-carbone dans les cycles de (b) aux atomes d'hydrogène liés au silicium dans (a) est compris entre 0,8:1 et 1,1:1.
7. Polymère organosilicié réticulable selon l'une quelconque des revendications 1 à 6, caractérisé en ce qu'il est thermoplastique et en ce que le rapport des doubles liaisons carbone-carbone dans les cycles de (b) aux atomes d'hydrogène liés au silicium dans (a) est supérieur à 0,5:1, pouvant atteindre une valeur de 0,7:1, ou est compris entre 1,3:1 et 1,8:1.
8. Utilisation du polymère organosilicié selon l'une quelconque des revendications précédentes dans une structure composite renforcée par des fibres comprenant jusqu'à 80% en poids de fibres de renforcement.
9. Utilisation selon la revendication 8 du polymère organosilicié, caractérisée en ce que les fibres de renforcement consistent en verre, carbone, métal, céramique, ou en fibres de polymère synthétique, ou en un mat de fibres.
10. Procédé pour préparer les polymères organosiliciés selon l'une quelconque des revendications 1 à 9, caractérisé en ce qu'il comprend la réaction, en présence d'un catalyseur contenant du platine, (a) d'un polysiloxane cyclique ou d'un tétra(siloxy)silane contenant comme sites réactifs au moins deux atomes d'hydrogène liés au silicium et (b) un polyène polycyclique, contenant comme sites réactifs au moins deux doubles liaisons carbone-carbone non aromatiques dans les cycles, par molécule, le rapport des doubles liaisons carbone-carbone dans les cycles de (b) aux atomes d'hydrogène liés au silicium dans (a) étant supérieur à 0,5:1 et pouvant atteindre une valeur de 1,8:1, et au moins l'un des réactifs (a) ou (b) ayant plus de deux sites réactifs, et l'application d'une chaleur audit polymère pour développer la réticulation jusqu'à un maximum.
11. Procédé de préparation de polymères organosiliciés selon la revendication 10, caractérisé en ce que le polysiloxane cyclique est :



dans laquelle R est un atome d'hydrogène, un radical alkyle ou alcoxy saturé, substitué ou non substitué, un radical aromatique ou aryloxy substitué ou non substitué, n est un nombre entier compris entre 3 et 20, et R est un atome d'hydrogène sur au moins deux des atomes de silicium dans la molécule; ou le tétra(siloxy)silane est



dans laquelle R est tel que défini ci-dessus et est un atome d'hydrogène sur au moins deux atomes de silicium dans la molécule.

12. Procédé de préparation de polymères organosiliciés selon la revendication 10, caractérisé en ce que le rapport des doubles liaisons carbone-carbone dans les cycles de (b) aux atomes d'hydrogène liés au

silicium dans (a) est compris entre 0,7:1 et 1,3:1.

13. Procédé de préparation de polymères organosiliciés selon la revendication 12, caractérisé en ce que le rapport des doubles liaisons carbone-carbone dans les cycles de (b) aux atomes d'hydrogène liés au silicium dans (a) est compris entre 0,8:1 et 1,1:1.

14. Procédé de préparation de polymères organosiliciés selon l'une quelconque des revendications 10 à 13, caractérisé en ce que le catalyseur contenant du platine est choisi parmi l'acide chloroplatinique, $PtCl_2$ et le dichlorure de dibenzonitrile platine.

15. Procédé de préparation de polymères organosiliciés selon l'une quelconque des revendications 10 à 14, caractérisé en ce qu'il comprend les étapes de : (i) réaction partielle de (a) et (b) pour former un prépolymère; (ii) transfert du prépolymère dans un moule; et (iii) durcissement du prépolymère pour former un produit thermodurci moulé.

Revendications pour l'Etat contractant suivant : ES

1. Procédé de préparation d'un polymère organosilicié réticulé ou réticulable comprenant en alternance (1) des restes hydrocarbonés polycycliques et (2) des restes polysiloxane cycliques ou tétra(siloxy)silane reliés par des liaisons carbonosilicium, caractérisé en ce qu'il comprend la réaction, en présence d'un catalyseur contenant du platine, (a) d'un polysiloxane cyclique ou d'un tétra(siloxy)silane contenant en tant que sites réactifs au moins deux atomes d'hydrogène liés au silicium et (b) un polyène polycyclique, contenant en tant que sites réactifs au moins deux doubles liaisons carbone-carbone non aromatiques dans les cycles, par molécule, le rapport des doubles liaisons carbone-carbone dans (b) aux atomes d'hydrogène liés au silicium dans les cycles de (a) étant supérieur à 0,5:1 et pouvant atteindre la valeur de 1,8:1, et au moins l'un des réactifs (a) ou (b) ayant plus de deux sites réactifs, et l'application audit polymère d'une chaleur pour développer la réticulation jusqu'à un maximum.

2. Procédé de préparation de polymères organosiliciés selon la revendication 1, caractérisé en ce que le polysiloxane cyclique est



dans laquelle R est un atome d'hydrogène, un radical alkyle ou alcoxy saturé, substitué ou non substitué, un radical aromatique ou aryloxy substitué ou non substitué, n est un nombre entier compris entre 3 et 20, et R est un atome d'hydrogène sur au moins deux des atomes de silicium dans la molécule; ou le tétra(siloxy)silane est :



dans laquelle R est tel que défini ci-dessus et est un atome d'hydrogène sur au moins deux atomes de silicium dans la molécule.

3. Procédé de préparation de polymères organosiliciés selon la revendication 1, caractérisé en ce que le rapport des doubles liaisons carbone-carbone dans les cycles de (b) aux atomes d'hydrogène liés au silicium dans (a) est compris entre 0,7:1 et 1,3:1.

5 4. Procédé de préparation de polymères organosiliciés selon la revendication 3, caractérisé en ce que le rapport des doubles liaisons carbone-carbone dans les cycles de (b) aux atomes d'hydrogène liés au silicium dans (a) est compris entre 0,8:1 et 1,1:1.

10 5. Procédé de préparation de polymères organosiliciés selon l'une quelconque des revendications 1 à 4, caractérisé en ce que le catalyseur contenant du platine est choisi parmi l'acide chloroplatinique, PtCl_2 et le dichlorure de dibenzonitrile platine.

15 6. Procédé de préparation de polymères organosiliciés selon l'une quelconque des revendications 1 à 5, caractérisé en ce qu'il comprend les étapes de : (i) réaction partielle de (a) et (b) pour former un prépolymère; (ii) transfert du prépolymère dans un moule; et (iii) durcissement du prépolymère pour former un produit thermodurci moulé.

20 7. Procédé de préparation de polymères organosiliciés selon l'une quelconque des revendications 1 à 6, caractérisé en ce que le polyène polycyclique est le norbornadiène, le dicyclopentadiène, le tricyclopentadiène, l'hexahydronaphtalène, le diméthano-hexahydronaphtalène, ou le norbornadiène dimère.

25 8. Utilisation du polymère organosilicié selon l'une quelconque des revendications précédentes dans une structure composite renforcée par des fibres comprenant jusqu'à 80% en poids de fibres de renforcement.

30 9. Utilisation selon la revendication 8 du polymère organosilicié, caractérisée en ce que les fibres de renforcement consistent en verre, carbone, métal, céramique, ou en fibres de polymère synthétique, ou en un mat de fibres.

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